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(71) Applicant: KIMBERLY-CLARK CORPORATION [US/US]; 401 North Lake Street, Neenah, WI 54956 (US).		<b>Published</b> <i>With international search report. Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i>
(72) Inventors: NOHR, Ronald, Sinclair, 452 Bellflower Court, Roswell, GA 30076 (US). MACDONALD, John, Gavin, 1472 Knollwood Terrace, Decatur, GA 30033 (US). MCGINNISS, Vincent, Daniel, 1315 North State Route 3, Sunbury, OH 43073 (US). WHITMORE, Robert, Samuel, Jr., 3763 Eisenhower Road, Columbus, OH 43224 (US).		
(74) Agents: MAYCOCK, William, E. et al.; Kimberly-Clark Corporation, 401 North Lake Street, Neenah, WI 54956 (US).		

(54) Title: MUTABLE COMPOSITION AND METHODS OF USE THEREOF

(57) Abstract

A colored composition which includes a colorant and an ultraviolet radiation transorber. The colorant, in the presence of the ultraviolet radiation transorber, is adapted, upon exposure of the transorber to ultraviolet radiation, to be mutable. The ultraviolet radiation transorber is adapted to absorb ultraviolet radiation and interact with the colorant to effect the irreversible mutation of the colorant. By way of example, the colored composition can be incorporated into a toner adapted to be utilized in an electrophotographic process. The toner includes the colorant, ultraviolet radiation transorber, and a carrier. The carrier can be a polymer, and the toner may contain a charge carrier. The ultraviolet radiation in general will have wavelengths of from about 100 to about 375 nanometers. Especially useful ultraviolet radiation is incoherent, pulsed ultraviolet radiation produced by a dielectric barrier discharge excimer lamp. In another embodiment, the colored composition which comprises a colorant and an ultraviolet radiation transorber may also contain a molecular includant having a chemical structure which defines at least one cavity. Each of the colorant and ultraviolet radiation transorber is associated with the molecular includant. In some embodiments, the colorant is at least partially included within a cavity of the molecular includant and the ultraviolet radiation transorber is associated with the molecular includant outside of the cavity. In other embodiments, the ultraviolet radiation transorber is covalently coupled to the molecular includant.

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## MUTABLE COMPOSITION AND METHODS OF USE THEREOF

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### Cross-reference to Related Application

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This application is a continuation-in-part application of U.S. Serial No. 08/119,912, filed September 10, 1993, and is a continuation-in-part application of Serial No. 08/103,503, filed on August 5, 1993.

### Technical Field

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The present invention relates to a mutable colored composition, which, in some embodiments, may be employed in an electrophotographic toner, e.g., a toner employed in a photocopier which is based on transfer xerography.

### Background of the Invention

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Electrophotography is broadly defined as a process in which photons are captured to create an electrical image analog of the original. The electrical analog, in turn, is manipulated through a number of steps which result in a physical image. The most common form of electrophotography presently in use is called transfer xerography. Although first demonstrated by C. Carlson in 1938, the process was slow to gain acceptance. Today, however, transfer xerography is the foundation of a multi-billion dollar industry.

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The heart of the process is a photoreceptor, usually the moving element of the process, which is typically either drum-shaped or a continuous, seamless belt. A corona discharge

device deposits gas ions on the photoreceptor surface. The ions provide a uniform electric field across the photoreceptor and a uniform charge layer on its surface. An image of an illuminated original is projected through a lens system and focused on the photoreceptor. Light striking the charged photoreceptor surface results in increased conductivity across the photoreceptor with the concomitant neutralization of surface charges. Unilluminated regions of the photoreceptor surface retain their charges. The resulting pattern of surface charges is the latent electrostatic image.

A thermoplastic pigmented powder or toner, the particles of which bear a charge opposite to the surface charges on the photoreceptor, is brought close to the photoreceptor, thereby permitting toner particles to be attracted to the charged regions on the photoreceptor surface. The result is a physical image on the photoreceptor surface consisting of electrostatically held toner particles.

A sheet of plain paper is brought into physical contact with the toner-bearing photoreceptor. A charge applied to the back side of the paper induces the attraction of the toner image to the paper. The image is a positive image of the original. The paper then is stripped from the photoreceptor, with the toner image clinging to it by electrostatic attraction. The toner image is permanently fused to the paper by an appropriate heating means, such as a hot pressure roll or a radiant heater.

Because there is incomplete transfer of toner to the paper, it is necessary to clean the photoreceptor surface of residual toner. Such toner is wiped off with a brush, cloth, or blade. A corona discharge or reverse polarity aids in the removal of toner. A uniform light source then floods the photoreceptor to neutralize any residual charges from the previous image cycle, erasing the previous electrostatic image completely and conditioning the photoreceptor surface for another cycle.

The toner generally consists of 1-15 micrometer average diameter particles of a thermoplastic powder. Black

toner typically contains 5-10 percent by weight of carbon black particles of less than 1 micrometer dispersed in the thermoplastic powder. For toners employed in color xerography, the carbon black may be replaced with cyan, magenta, or yellow pigments.

5 The concentration and dispersion of the pigment must be adjusted to impart a conductivity to the toner which is appropriate for the development system. For most development processes, the toner is required to retain for extended periods of time the charge applied by contact electrification. The thermoplastic employed in  
10 the toner in general is selected on the basis of its melting behavior. The thermoplastic must melt over a relatively narrow temperature range, yet be stable during storage and able to withstand the vigorous agitation which occurs in xerographic development chambers.

15 The success of electrophotography, and transfer xerography in particular, no doubt is a significant factor in the efficient distribution of information which has become essential in a global setting. It also contributes to the generation of vast quantities of paper which ultimately must either be disposed of or  
20 recycled. Although the technology for recycling paper exists, it is costly, time consuming, and generates waste which must be appropriately disposed of. The conventional method for recycling paper comprises converting paper to pulp, and treating the pulp to remove ink, toner, and other colored materials, i.e.,  
25 "de-inking" the paper, an expensive and not always completely successful operation. Moreover, de-inking results in a sludge which typically is disposed of in a landfill. The resulting de-inked pulp then is used, often with the addition of at least some virgin pulp, to form paper, cardboard, cellulosic packaging materials,  
30 and the like.

The simplest form of recycling, however, would be to reuse the paper intact, thus eliminating the need to re-pulp. To this end, toners for copier machines have been reported which are rendered colorless on exposure to near infrared or infrared  
35 radiation. Although the lower wavelength end of the spectrum of

sunlight ends at about 375 nanometers. it has a significant infrared component at the upper wavelength end of the spectrum. Hence, such toners have a salient disadvantage in that they are transitory in the presence of such environmental factors as sunlight and heat; that is, such toners become colorless. This result is unsatisfactory because the documents can be rendered illegible before their function or purpose has ended. Accordingly, there is a need for toners for copy machines which will permit the recycling of paper intact, but which are stable to normally encountered environmental factors.

### Summary of the Invention

The present invention addresses the need for a simple, cost-effective, and environmentally sound method for recycling paper and for the multiple reuse of photocopy paper.

The present invention provides, in general, a colorant system that is mutable by exposure to radiation. More particularly, the present invention provides a composition comprising a colorant which, in the presence of a radiation transorber, is mutable. The radiation transorber is capable of absorbing radiation and interacting with the colorant to effect a mutation of the colorant. In addition, it is desirable that the mutation of the colorant be irreversible.

The composition of the present invention includes a colorant and an ultraviolet radiation transorber. The colorant, in the presence of the ultraviolet radiation transorber, is adapted, upon exposure of the transorber to ultraviolet radiation, to be mutable. The ultraviolet radiation transorber is adapted to absorb ultraviolet radiation and interact with the colorant to effect the irreversible mutation of the colorant. It is desirable that the ultraviolet radiation transorber absorb ultraviolet radiation at a wavelength of from about 4 to about 400 nanometers. It is even more desirable that the ultraviolet radiation transorber absorb ultraviolet radiation at a wavelength of 100 to 375 nanometers.

In another embodiment of the present invention, the colored composition which comprises a colorant and an ultraviolet radiation transorber may also contain a molecular includant having a chemical structure which defines at least one cavity. The molecular includants include, but are not limited to, clathrates, zeolites, and cyclodextrins. Each of the colorant and ultraviolet radiation transorber is associated with one or more molecular includant. In some embodiments, the colorant is at least partially included within a cavity of the molecular includant and the ultraviolet radiation transorber is associated with the molecular includant outside of the cavity. In some embodiments, the ultraviolet radiation transorber is covalently coupled to the outside of the molecular includant.

The present invention also relates to a method of mutating the colorant in the composition of the present invention. The method comprises irradiating a composition containing a mutable colorant and an ultraviolet radiation transorber with ultraviolet radiation at a dosage level sufficient to mutate the colorant. As stated above, in some embodiments, the composition further includes a molecular includant. In another embodiment, the composition is applied to a substrate before being irradiated with ultraviolet radiation. It is desirable that the mutated colorant is stable. The present invention is also related to a substrate having an image thereon that is formed by the composition of the present invention.

The present invention is also related to an electrophotographic method that allows for the multiple reuse of a substrate such as photocopy paper. The method comprises exposing an image on a substrate as produced above, to ultraviolet radiation at a dosage level sufficient to irreversibly mutate the colorant. Next, a second image is created on a photoreceptor surface, and a second toner is applied to the photoreceptor surface to form a toner image which replicates the second image. Then the second toner image of the second image is transferred to the substrate, and the second toner image is fixed to the substrate.

Where the second toner contains a colorant and a ultraviolet radiation transorber of the present invention, then the colorant in the second image may also be mutated by exposure to ultraviolet radiation, thus allowing the substrate to be reused for the fixation of a third image to the substrate.

These and other objects, features and advantages of the present invention will become apparent after a review of the following detailed description of the disclosed embodiments and the appended claims.

### Brief Description of the Figures

Figure 1 illustrates an ultraviolet radiation transorber/ mutable colorant/ molecular includant complex wherein the mutable colorant is malachite green, the ultraviolet radiation transorber is Irgacure 184 (1-hydroxycyclohexyl phenyl ketone), and the molecular includant is  $\beta$ -cyclodextrin.

Figure 2 illustrates an ultraviolet radiation transorber/ mutable colorant/ molecular includant complex wherein the mutable colorant is victoria pure blue BO (Basic Blue 7) , the ultraviolet radiation transorber is Irgacure 184 (1-hydroxycyclohexyl phenyl ketone), and the molecular includant is  $\beta$ -cyclodextrin.

Figure 3 is an illustration of several 222 nanometer excimer lamps arranged in four parallel columns wherein the twelve numbers represent the locations where twelve intensity measurements were obtained approximately 5.5 centimeters from the excimer lamps.

Figure 4 is an illustration of several 222 nanometer excimer lamps arranged in four parallel columns wherein the nine numbers represent the locations where nine intensity



measurements were obtained approximately 5.5 centimeters from the excimer lamps.

Figure 5 is an illustration of several 222 nanometer excimer lamps arranged in four parallel columns wherein the location of the number "1" denotes the location where ten intensity measurements were obtained from increasing distances from the lamps at that location. (The measurements and their distances from the lamp are summarized in Table 7.)

#### Detailed Description of the Invention

The present invention relates in general to a colorant system that is mutable by exposure to radiation. The present invention relates to a composition comprising a colorant which, in the presence of a radiation transorber, is mutable. The radiation transorber is capable of absorbing radiation and interacting with the colorant to effect a mutation of the colorant.

More particularly, the composition of the present invention includes a colorant and an ultraviolet radiation transorber. The colorant, in the presence of the ultraviolet radiation transorber, is adapted, upon exposure of the transorber to ultraviolet radiation, to be mutable. The ultraviolet radiation transorber is adapted to absorb ultraviolet radiation and interact with the colorant to effect the irreversible mutation of the colorant. The term "composition" and such variations as "colored composition" are used herein to mean a colorant, and an ultraviolet radiation transorber. When reference is being made to a colored composition which is adapted for a specific application, such as a toner to be used in an electrophotographic process, the term "composition-based" is used as a modifier to indicate that the material, e.g., a toner, includes a colorant, an ultraviolet radiation transorber, and, optionally, a molecular includant.

As used herein, the term "colorant" is meant to include, without limitation, any material which, in the presence of an ultraviolet radiation transorber, is adapted upon exposure to

ultraviolet radiation to be mutable. The colorant typically will be an organic material, such as an organic dye or pigment, including toners and lakes. Desirably, the colorant will be substantially transparent to, that is, will not significantly interact with, the ultraviolet radiation to which it is exposed. The term is meant to include a single material or a mixture of two or more materials.

Organic dye classes include, by way of illustration only, triaryl methyl dyes, such as Malachite Green Carbinol base {4-(dimethylamino)- $\alpha$ -[4-(dimethylamino)phenyl]- $\alpha$ -phenyl-benzene-methanol}, Malachite Green Carbinol hydrochloride {N-4-[[4-(dimethylamino)phenyl]-phenylmethylene]-2,5-cyclohexyldien-1-ylidene]-N-methyl-methanaminium chloride or bis[p-(dimethylamino)phenyl]phenylmethylium chloride}, and Malachite Green oxalate {N-4-[[4-(dimethylamino)phenyl]phenylmethylene]-2,5-cyclohexyldien-1-ylidene]-N-methylmethanaminium chloride or bis[p-(dimethylamino)phenyl]phenylmethylium oxalate}; monoazo dyes, such as Cyanine Black, Chrysoidine [Basic Orange 2; 4-(phenylazo)-1,3-benzenediamine monohydrochloride], and B-Naphthol Orange; thiazine dyes, such as Methylene Green, zinc chloride double salt [3,7-bis(dimethylamino)-6-nitrophenothiazin-5-ium chloride, zinc chloride double salt]; oxazine dyes, such as Lumichrome (7,8-dimethylalloxazine); naphthalimide dyes, such as Lucifer Yellow CH {6-amino-2-[(hydrazinocarbonyl)amino]-2,3-dihydro-1,3-dioxo-1H-benz[de]isoquinoline-5,8-disulfonic acid dilithium salt}; azine dyes, such as Janus Green B {3-(diethylamino)-7-[[4-(dimethylamino)phenyl]azo]-5-phenylphenazinium chloride}; cyanine dyes, such as Indocyanine Green {Cardio-Green or Fox Green; 2-[7-[1,3-dihydro-1,1-dimethyl-3-(4-sulfobutyl)-2H-benz[e]indol-2-ylidene]-1,3,5-heptatrienyl]-1,1-dimethyl-3-(4-sulfobutyl)-1H-benz[e]indolium hydroxide inner salt sodium salt}; indigo dyes, such as Indigo {Indigo Blue or Vat Blue 1; 2-(1,3-dihydro-3-oxo-2H-indol-2-ylidene)-1,2-dihydro-3H-indol-3-one}; coumarin dyes, such as 7-hydroxy-4-methylcoumarin (4-methylumbelliferone); benzimidazole dyes, such as Hoechst 33258

[bisbenzimidazole or 2-(4-hydroxyphenyl)-5-(4-methyl-1-piperazinyl)-2,5-bis-1H-benzimidazole trihydrochloride pentahydrate]; paraquinoidal dyes, such as Hematoxylin {Natural Black 1; 7,11-bis-dihydrobenz[b]indeno[1,2-d]pyran-3,4,6a,9,10(6H)-pentol};

5 fluorescein dyes, such as Fluoresceinamine (5-aminofluorescein); diazonium salt dyes, such as Diazo Red RC (Azoic Diazo No. 10 or Fast Red RC salt; 2-methoxy-5-chlorobenzenediazonium chloride, zinc chloride double salt); azoic diazo dyes, such as Fast

10 Blue BB salt (Azoic Diazo No. 20; 4-benzoylamino-2,5-diethoxybenzene diazonium chloride, zinc chloride double salt); phenylenediamine dyes, such as Disperse Yellow 9 [N-(2,4-dinitrophenyl)-1,4-phenylenediamine or Solvent Orange 53]; diazo dyes, such as Disperse Orange 13 [Solvent Orange 52; 1-phenylazo-4-(4-hydroxyphenylazo)naphthalene]; anthraquinone

15 dyes, such as Disperse Blue 3 [Celliton Fast Blue FFR; 1-methylamino-4-(2-hydroxyethylamino)-9,10-anthraquinone], Disperse Blue 14 [Celliton Fast Blue B; 1,4-bis(methylamino)-9,10-anthraquinone], and Alizarin Blue Black B (Mordant Black 13); trisazo dyes, such as Direct Blue 71 (Benzo Light Blue FFL or Sirius Light Blue BRR; 3-[(4-[(4-[(6-amino-1-hydroxy-3-sulfo-2-naphthalenyl)azo]-6-sulfo-1-naphthalenyl)azo]-1-naphthalenyl)azo]-1,5-naphthalenedisulfonic acid tetrasodium salt);

20 xanthene dyes, such as 2,7-dichlorofluorescein; proflavine dyes, such as 3,6-diaminoacridine hemisulfate (Proflavine);

25 sulfonaphthalein dyes, such as Cresol Red (o-cresolsulfonaphthalein); phthalocyanine dyes, such as Copper Phthalocyanine {Pigment Blue 15; (SP-4-1)-[29H,31H-phthalocyanato(2-)-N<sup>29</sup>,N<sup>30</sup>,N<sup>31</sup>,N<sup>32</sup>]copper}; carotenoid dyes, such as *trans*- $\beta$ -carotene (Food Orange 5); carminic acid dyes,

30 such as Carmine, the aluminum or calcium-aluminum lake of carminic acid (7-a-D-glucopyranosyl-9,10-dihydro-3,5,6,8-tetrahydroxy-1-methyl-9,10-dioxo-2-anthracenecarboxylic acid); azure dyes, such as Azure A [3-amino-7-(dimethylamino)phenothiazin-5-ium chloride or 7-(dimethylamino)-3-imino-3H-phenothiazine hydrochloride]; and

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acridine dyes, such as Acridine Orange [Basic Orange 14; 3,8-bis(dimethylamino)acridine hydrochloride, zinc chloride double salt] and Acriflavine (Acriflavine neutral; 3,6-diamino-10-methylacridinium chloride mixture with 3,6-acridinediamine).

5           The term "mutable" with reference to the colorant is used to mean that the absorption maximum of the colorant in the visible region of the electromagnetic spectrum is capable of being mutated or changed by exposure to ultraviolet radiation when in the presence of the ultraviolet radiation transorber. In general, it is only necessary that such absorption maximum be mutated to an absorption maximum which is different from that of the colorant prior to exposure to the ultraviolet radiation, and that the mutation be irreversible. Thus, the new absorption maximum can be within or outside of the visible region of the electromagnetic spectrum. In other words, the colorant can mutate to a different color or be rendered colorless. The latter, of course, is desirable when the colorant is used in a colored composition adapted to be utilized as a toner in an electrophotographic process which reuses the electrophotographic copy by first rendering the colored composition colorless and then placing a new image thereon.

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          As used herein, the term "irreversible" means that the colorant will not revert to its original color when it no longer is exposed to ultraviolet radiation. Desirably, the mutated colorant will be stable, i.e., not appreciably adversely affected by radiation normally encountered in the environment, such as natural or artificial light and heat. Thus, desirably, a colorant rendered colorless will remain colorless indefinitely.

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          The term "ultraviolet radiation transorber" is used herein to mean any material which is adapted to absorb ultraviolet radiation and interact with the colorant to effect the mutation of the colorant. In some embodiments, the ultraviolet radiation transorber may be an organic compound. The term "compound" is intended to include a single material or a mixture of two or more materials. If two or more materials are employed, it is not

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necessary that all of them absorb ultraviolet radiation of the same wavelength.

5 The present invention includes unique compounds that are capable of absorbing narrow ultraviolet wavelength radiation. The compounds are synthesized by combining a wavelength-selective sensitizer and a photoreactor. The photoreactors oftentimes do not efficiently absorb high energy radiation. When combined with the wavelength-selective sensitizer, the resulting compound is a wavelength specific  
10 compound that efficiently absorbs a very narrow spectrum of radiation. Examples of ultraviolet radiation transorbers are shown in Examples 5 and 9 herein.

15 While the mechanism of the interaction of the ultraviolet radiation transorber with the colorant is not totally understood, it is believed that it may interact with the colorant in a variety of ways. For example, the ultraviolet radiation transorber, upon absorbing ultraviolet radiation, may be converted to one or more free radicals which interact with the colorant. Such free radical-generating compounds typically are  
20 hindered ketones, some examples of which include, but are not limited to: benzildimethyl ketal (available commercially as Irgacure® 651, Ciba-Geigy Corporation, Hawthorne, New York); 1-hydroxycyclohexyl phenyl ketone (Irgacure® 500); 2-methyl-1-[4-(methylthio)phenyl]-2-morpholino-propan-1-one (Irgacure®  
25 907); 2-benzyl-2-dimethylamino-1-(4-morpholinophenyl)butan-1-one (Irgacure® 369); and 1-hydroxycyclohexyl phenyl ketone (Irgacure® 184).

Alternatively, the ultraviolet radiation may initiate an electron transfer or reduction-oxidation reaction between the  
30 ultraviolet radiation transorber and the colorant. In this case, the ultraviolet radiation transorber may be, but is not limited to, Michler's ketone (p-dimethylaminophenyl ketone) or benzyl trimethyl stannate. Or, a cationic mechanism may be involved, in which case the ultraviolet radiation transorber could be, for  
35 example, bis[4-(diphenylsulphonio)phenyl]] sulfide bis-

(hexafluorophosphate) (Degacure® KI85, Ciba-Geigy Corporation, Hawthorne, New York); Cyracure® UVI-6990 (Ciba-Geigy Corporation), which is a mixture of bis[4-(diphenylsulphonio)phenyl] sulfide bis(hexafluorophosphate) with  
5 related monosulphonium hexafluorophosphate salts; and 5-2,4-(cyclopentadienyl)[1,2,3,4,5,6-(methylethyl)benzene]-iron(II) hexafluorophosphate (Irgacure® 261).

The term "ultraviolet radiation" is used herein to mean electromagnetic radiation having wavelengths in the range  
10 of from about 4 to about 400 nanometers. The especially desirable ultraviolet radiation range for the present invention is between approximately 100 to 375 nanometers. Thus, the term includes the regions commonly referred to as ultraviolet and vacuum ultraviolet. The wavelength ranges typically assigned to  
15 these two regions are from about 180 to about 400 nanometers and from about 100 to about 180 nanometers, respectively.

In some embodiments, the molar ratio of ultraviolet radiation transorber to colorant generally will be equal to or greater than about 0.5. As a general rule, the more efficient the  
20 ultraviolet radiation transorber is in absorbing the ultraviolet radiation and interacting with, i.e., transferring absorbed energy to, the colorant to effect irreversible mutation of the colorant, the lower such ratio can be. Current theories of molecular photo chemistry suggest that the lower limit to such ratio is 0.5, based  
25 on the generation of two free radicals per photon. As a practical matter, however, ratios higher than 1 are likely to be required, perhaps as high as about 10. However, the present invention is not bound by any specific molar ratio range. The important feature is that the transorber is present in an amount sufficient to  
30 effect mutation of the colorant.

As a practical matter, the colorant, and ultraviolet radiation transorber are likely to be solids. However, any or all of such materials can be a liquid. In an embodiment where the colored composition of the present invention is a solid, the  
35 effectiveness of the ultraviolet radiation transorber is improved

when the colorant and ultraviolet radiation transorber are in intimate contact. To this end, the thorough blending of the two components, along with other components which may be present, is desirable. Such blending generally is accomplished by any of the means known to those having ordinary skill in the art. When the colored composition includes a polymer, blending is facilitated if the colorant and the ultraviolet radiation transorber are at least partly soluble in softened or molten polymer. In such case, the composition is readily prepared in, for example, a two-roll mill. Alternatively, the colored composition can be a liquid because one or more of its components is a liquid.

For some applications, the colored composition of the present invention typically will be utilized in particulate form. In other applications, the particles of the composition should be very small. For example, the particles of a colored composition adapted for use as a toner in an electrophotographic process typically consist of 7-15 micrometer average diameter particles, although smaller or larger particles can be employed. It is important to note that the particles should be as uniform in size as possible. Methods of forming such particles are well known to those having ordinary skill in the art.

Photochemical processes involve the absorption of light quanta, or photons, by a molecule, e.g., the ultraviolet radiation transorber, to produce a highly reactive electronically excited state. However, the photon energy, which is proportional to the wavelength of the radiation, cannot be absorbed by the molecule unless it matches the energy difference between the unexcited, or original, state and an excited state. Consequently, while the wavelength range of the ultraviolet radiation to which the colored composition is exposed is not directly of concern, at least a portion of the radiation must have wavelengths which will provide the necessary energy to raise the ultraviolet radiation transorber to an energy level which is capable of interacting with the colorant.

It follows, then, that the absorption maximum of the ultraviolet radiation transorber ideally will be matched with the wavelength range of the ultraviolet radiation in order to increase the efficiency of the mutation of the colorant. Such efficiency  
5 also will be increased if the wavelength range of the ultraviolet radiation is relatively narrow, with the maximum of the ultraviolet radiation transorber coming within such range. For these reasons, especially suitable ultraviolet radiation has a wavelength of from about 100 to about 375 nanometers.  
10 Ultraviolet radiation within this range desirably may be incoherent, pulsed ultraviolet radiation from a dielectric barrier discharge excimer lamp.

The term "incoherent, pulsed ultraviolet radiation" has reference to the radiation produced by a dielectric barrier discharge excimer lamp (referred to hereinafter as "excimer  
15 lamp"). Such a lamp is described, for example, by U. Kogelschatz, "Silent discharges for the generation of ultraviolet and vacuum ultraviolet excimer radiation," *Pure & Appl. Chem.*, 62, No. 9, pp. 1667-1674 (1990); and E. Eliasson and U. Kogelschatz, "UV Excimer Radiation from Dielectric-Barrier  
20 Discharges," *Appl. Phys. B*, 46, pp. 299-303 (1988). Excimer lamps were developed originally by ABB Infocom Ltd., Lenzburg, Switzerland. The excimer lamp technology since has been acquired by Heraeus Noblelight AG, Hanau, Germany.

The excimer lamp emits radiation having a very narrow bandwidth, i.e., radiation in which the half width is of the order of 5-15 nanometers. This emitted radiation is incoherent and pulsed, the frequency of the pulses being dependent upon the frequency of the alternating current power supply which typically  
25 is in the range of from about 20 to about 300 kHz. An excimer lamp typically is identified or referred to by the wavelength at which the maximum intensity of the radiation occurs, which convention is followed throughout this specification. Thus, in comparison with most other commercially useful sources of  
30 ultraviolet radiation which typically emit over the entire  
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- 15 -

ultraviolet spectrum and even into the visible region. excimer lamp radiation is substantially monochromatic.

Excimers are unstable molecular complexes which occur only under extreme conditions, such as those temporarily existing in special types of gas discharge. Typical examples are the molecular bonds between two rare gaseous atoms or between a rare gas atom and a halogen atom. Excimer complexes dissociate within less than a microsecond and, while they are dissociating, release their binding energy in the form of ultraviolet radiation. Known excimers, in general, emit in the range of from about 125 to about 360 nanometers, depending upon the excimer gas mixture.

Although the colorant and the ultraviolet radiation transorber have been described as separate compounds, they can be part of the same molecule. For example, they can be covalently coupled to each other, either directly, or indirectly through a relatively small molecule, or spacer. Alternatively, the colorant and ultraviolet radiation transorber can be covalently coupled to a large molecule, such as an oligomer or a polymer, particularly when the solid colored composition of the present invention is adapted to be utilized as a toner in an electrophotographic process. Further, the colorant and ultraviolet radiation transorber may be associated with a large molecule by van der Waals forces, and hydrogen bonding, among other means. Other variations will be readily apparent to those having ordinary skill in the art.

For example, in an embodiment of the composition of the present invention, the composition further comprises a molecular includant. The term "molecular includant," as used herein, is intended to mean any substance having a chemical structure which defines at least one cavity. That is, the molecular includant is a cavity-containing structure. As used herein, the term "cavity" is meant to include any opening or space of a size sufficient to accept at least a portion of one or both of the colorant and the ultraviolet radiation transorber. Thus, the cavity

can be a tunnel through the molecular includant or a cave-like space in the molecular includant. The cavity can be isolated or independent, or connected to one or more other cavities.

5 The molecular includant can be inorganic or organic in nature. In certain embodiments, the chemical structure of the molecular includant is adapted to form a molecular inclusion complex. Examples of molecular includants are, by way of illustration only, clathrates or intercalates, zeolites, and cyclodextrins. Examples of cyclodextrins include, but are not  
10 limited to, alpha-cyclodextrin, beta-cyclodextrin, gamma-cyclodextrin, hydroxypropyl beta-cyclodextrin, hydroxyethyl beta-cyclodextrin, sulfated beta-cyclodextrin, and sulfated gamma-cyclodextrin. (American Maize-Products Company, of Hammond Indiana) In some embodiments, the molecular  
15 includant is a cyclodextrin. More particularly, in some embodiments, the molecular includant is an alpha-cyclodextrin. In other embodiments, the molecular includant is a beta-cyclodextrin. Although not wanting to be bound by the following theory, it is believed that the closer the transorber molecule is to  
20 the mutable colorant on the molecular includant, the more efficient the interaction with the colorant to effect mutation of the colorant. Thus, the molecular includant with functional groups that can react with and bind the transorber molecule and that are close to the binding site of the mutable colorant are the more  
25 desirable molecular includants.

The colorant and the ultraviolet radiation transorber are associated with the molecular includant. The term "associated" in its broadest sense means that the colorant and the ultraviolet radiation transorber are at least in close proximity to  
30 the molecular includant. For example, the colorant and/or the ultraviolet radiation transorber can be maintained in close proximity to the molecular includant by hydrogen bonding, van der Waals forces, or the like. Alternatively, either or both of the colorant and the ultraviolet radiation transorber can be covalently  
35 bonded to the molecular includant. In certain embodiments, the

colorant will be associated with the molecular includant by means of hydrogen bonding and/or van der Waals forces or the like, while the ultraviolet radiation transorber is covalently bonded to the molecular includant. In other embodiments, the colorant is at least partially included within the cavity of the molecular includant, and the ultraviolet radiation transorber is located outside of the cavity of the molecular includant.

In one embodiment wherein the colorant and the ultraviolet radiation transorber are associated with the molecular includant, the colorant is crystal violet, the ultraviolet radiation transorber is a dehydrated phthaloylglycine-2959, and the molecular includant is beta-cyclodextrin. In yet another embodiment wherein the colorant and the ultraviolet radiation transorber are associated with the molecular includant, the colorant is crystal violet, the ultraviolet radiation transorber is 4(4-hydroxyphenyl) butan-2-one-2959 (chloro substituted), and the molecular includant is beta-cyclodextrin.

In another embodiment wherein the colorant and the ultraviolet radiation transorber are associated with the molecular includant, the colorant is malachite green, the ultraviolet radiation transorber is Irgacure 184, and the molecular includant is beta-cyclodextrin as shown in Figure 1. In still another embodiment wherein the colorant and the ultraviolet radiation transorber are associated with the molecular includant, the colorant is victoria pure blue BO, the ultraviolet radiation transorber is Irgacure 184, and the molecular includant is beta-cyclodextrin as shown in Figure 2.

Examples 5 through 9 disclose a method of preparing and associating these colorants and ultraviolet radiation transorbers to beta-cyclodextrins. It is to be understood that the methods disclosed in Examples 5 through 9 are merely one way of preparing and associating these components, and that many other methods known in the chemical arts may be used. Other methods of preparing and associated such components, or any of the other components which may be used in the present invention,

would be known to those of ordinary skill in the art once the specific components have been selected.

As a practical matter, the colorant, ultraviolet radiation transorber, and molecular includant are likely to be solids. However, any or all of such materials can be a liquid. The colored composition can be a liquid either because one or more of its components is a liquid, or, when the molecular includant is organic in nature, a solvent is employed. Suitable solvents include, but are not limited to, amides, such as N,N-dimethylformamide; sulfoxides, such as dimethylsulfoxide; ketones, such as acetone, methyl ethyl ketone, and methyl butyl ketone; aliphatic and aromatic hydrocarbons, such as hexane, octane, benzene, toluene, and the xylenes; esters, such as ethyl acetate; water; and the like. When the molecular includant is a cyclodextrin, particularly suitable solvents are the amides and sulfoxides.

The present invention also relates to a method of mutating the colorant in the composition of the present invention. Briefly described, the method comprises irradiating a composition containing a mutable colorant and an ultraviolet radiation transorber with ultraviolet radiation at a dosage level sufficient to mutate the colorant. As stated above, in one embodiment the composition further includes a molecular includant. In another embodiment, the composition is applied to a substrate before being irradiated with ultraviolet radiation.

The amount or dosage level of ultraviolet radiation that the colorant of the present invention is exposed to will generally be that amount which is necessary to mutate the colorant. The amount of ultraviolet radiation necessary to mutate the colorant can be determined by one of ordinary skill in the art using routine experimentation. Power density is the measure of the amount of radiated electromagnetic power traversing a unit area and is usually expressed in watts per centimeter squared ( $\text{W}/\text{cm}^2$ ). The power density level range is between approximately  $5 \text{ mW}/\text{cm}^2$  and  $15 \text{ mW}/\text{cm}^2$ , more particularly 8

to 10 mW/cm<sup>2</sup>. The dosage level, in turn, typically is a function of the time of exposure and the intensity or flux of the radiation source which irradiates the colored composition. The latter is effected by the distance of the composition from the source and, depending upon the wavelength range of the ultraviolet radiation, can be effected by the atmosphere between the radiation source and the composition. Accordingly, in some instances it may be appropriate to expose the composition to the radiation in a controlled atmosphere or in a vacuum, although in general neither approach is desired.

For example, in one embodiment, the colorant of the present invention is mutated by exposure to 222 nanometer excimer lamps. More particularly, the colorant crystal violet is mutated by exposure to 222 nanometer lamps. Even more particularly, the colorant crystal violet is mutated by exposure to 222 nanometer excimer lamps located approximately 5 to 6 centimeters from the colorant, wherein the lamps are arranged in four parallel columns approximately 30 centimeters long as shown in Figures 3 and 4. It is to be understood that the arrangement of the lamps is not critical to this aspect of the invention. Accordingly, one or more lamps may be arranged in any configuration and at any distance which results in the colorant mutating upon exposure to the lamp's ultraviolet radiation. One of ordinary skill in the art would be able to determine by routine experimentation which configurations and which distances are appropriate. Also, it is to be understood that different excimer lamps are to be used with different ultraviolet radiation transorbers. The excimer lamp used to mutate a colorant associated with an ultraviolet radiation transorber should produce ultraviolet radiation of a wavelength that is absorbed by the ultraviolet radiation transorber.

The colored composition of the present invention can be utilized on or in any substrate. If the composition is present in a substrate, however, the substrate should be substantially transparent to the ultraviolet radiation which is employed to

mutate the colorant. That is, the ultraviolet radiation will not significantly interact with or be absorbed by the substrate. As a practical matter, the composition typically will be placed on a substrate, with the most common substrate being paper. Other  
5 substrates, including, but not limited to, woven and nonwoven webs or fabrics, films, and the like, can be used, however.

Another aspect of the present invention is the substrate having an image thereon that is formed by the composition of the present invention. Although the present  
10 invention relates to any substrate capable of having a colored image fixed thereto, a desirable substrate is paper. Especially desirable substrates include, but are not limited to, photocopy paper and facsimile paper.

By way of example, the composition of the present  
15 invention can be incorporated into a toner adapted to be utilized in an electrophotographic process. The toner includes the colorant, ultraviolet radiation transorber, and a carrier. The carrier can be a polymer, and the toner may further contain a charge carrier. Briefly described, the electrophotographic  
20 process comprises the steps of creating an image on a photoreceptor surface, applying toner to the photoreceptor surface to form a toner image which replicates the image, transferring the toner image to a substrate, and fixing the toner image to the substrate. After the toner has been fixed on the  
25 substrate, the colorant in the composition is mutated by irradiating the substrate with ultraviolet radiation at a dosage level sufficient to irreversibly mutate the colorant. In some embodiments, the ultraviolet radiation used in the method to mutate the colorant will have wavelengths of from about 100 to  
30 about 375 nanometers. In other embodiments, the ultraviolet radiation is incoherent, pulsed ultraviolet radiation produced by a dielectric barrier discharge excimer lamp. In another embodiment, the toner may further comprise a molecular inculdant.

When the colored composition is adapted to be utilized as a toner in an electrophotographic process, the composition also will contain a carrier, the nature of which is well known to those having ordinary skill in the art. For many applications, the carrier will be a polymer, typically a thermosetting or thermoplastic polymer, with the latter being the more common.

Further examples of thermoplastic polymers include, but are not limited to: end-capped polyacetals, such as poly(oxymethylene) or polyformaldehyde, poly(trichloroacetaldehyde), poly(*n*-valeraldehyde), poly(acetaldehyde), poly(propionaldehyde), and the like; acrylic polymers, such as polyacrylamide, poly(acrylic acid), poly(methacrylic acid), poly(ethyl acrylate), poly(methyl methacrylate), and the like; fluorocarbon polymers, such as poly(tetrafluoroethylene), perfluorinated ethylenepropylene copolymers, ethylenetetrafluoroethylene copolymers, poly(chlorotrifluoroethylene), ethylene-chlorotrifluoroethylene copolymers, poly(vinylidene fluoride), poly(vinyl fluoride), and the like; epoxy resins, such as the condensation products of epichlorohydrin and bisphenol A; polyamides, such as poly(6-aminocaproic acid) or poly(E-caprolactam), poly(hexamethylene adipamide), poly(hexamethylene sebacamide), poly(11-aminoundecanoic acid), and the like; polyaramides, such as poly(imino-1,3-phenyleneiminoisophthaloyl) or poly(*m*-phenylene isophthalamide), and the like; parylenes, such as poly-*p*-xylylene, poly(chloro-*p*-xylylene), and the like; polyaryl ethers, such as poly(oxy-2,6-dimethyl-1,4-phenylene) or poly(*p*-phenylene oxide), and the like; polyaryl sulfones, such as poly(oxy-1,4-phenylenesulfonyl-1,4-phenyleneoxy-1,4-phenylene-isopropylidene-1,4-phenylene), poly(sulfonyl-1,4-phenyleneoxy-1,4-phenylenesulfonyl-4,4-biphenylene), and the like; polycarbonates, such as poly(bisphenol A) or poly(carbonyldioxy-1,4-phenyleneisopropylidene-1,4-phenylene), and the like; polyesters, such as poly(ethylene terephthalate),

poly(tetramethylene terephthalate), poly(cyclohexylene-1,4-dimethylene terephthalate) or poly(oxymethylene-1,4-cyclohexylenemethyleneoxyterephthaloyl), and the like; polyaryl sulfides, such as poly(p-phenylene sulfide) or poly(thio-1,4-phenylene), and the like; polyimides, such as poly(pyromellitimido-1,4-phenylene), and the like; polyolefins, such as polyethylene, polypropylene, poly(1-butene), poly(2-butene), poly(1-pentene), poly(2-pentene), poly(3-methyl-1-pentene), poly(4-methyl-1-pentene), 1,2-poly-1,3-butadiene, 1,4-poly-1,3-butadiene, polyisoprene, polychloroprene, polyacrylonitrile, poly(vinyl acetate), poly(vinylidene chloride), polystyrene, and the like; and copolymers of the foregoing, such as acrylonitrile-butadienestyrene (ABS) copolymers, styrene-*n*-butylmethacrylate copolymers, ethylene-vinyl acetate copolymers, and the like.

Some of the more commonly used thermoplastic polymers include styrene-*n*-butyl methacrylate copolymers, polystyrene, styrene-*n*-butyl acrylate copolymers, styrene-butadiene copolymers, polycarbonates, poly(methyl methacrylate), poly(vinylidene fluoride), polyamides (nylon-12), polyethylene, polypropylene, ethylene-vinyl acetate copolymers, and epoxy resins.

Examples of thermosetting polymers include, but are not limited to, alkyd resins, such as phthalic anhydride-glycerol resins, maleic acid-glycerol resins, adipic acid-glycerol resins, and phthalic anhydride-pentaerythritol resins; allylic resins, in which such monomers as diallyl phthalate, diallyl isophthalate, diallyl maleate, and diallyl chloroendate serve as nonvolatile cross-linking agents in polyester compounds; amino resins, such as aniline-formaldehyde resins, ethylene urea-formaldehyde resins, dicyandiamide-formaldehyde resins, melamine-formaldehyde resins, sulfonamide-formaldehyde resins, and urea-formaldehyde resins; epoxy resins, such as cross-linked epichlorohydrin-bisphenol A resins; phenolic resins, such as phenol-formaldehyde resins, including Novolacs and resols; and thermosetting polyesters, silicones, and urethanes.



In addition to the colorant, and ultraviolet radiation transorber, and optional carrier, the colored composition of the present invention also can contain additional components, depending upon the application for which it is intended. For example, a composition which is to be utilized as a toner in an electrophotographic process optionally can contain, for example, charge carriers, stabilizers against thermal oxidation, viscoelastic properties modifiers, cross-linking agents, plasticizers, and the like. Further, a composition which is to be utilized as a toner in an electrophotographic process optionally can contain charge control additives such as a quaternary ammonium salt; flow control additives such as hydrophobic silica, zinc stearate, calcium stearate, lithium stearate, polyvinylstearate, and polyethylene powders; and fillers such as calcium carbonate, clay and talc, among other additives used by those having ordinary skill in the art. For some applications, the charge carrier will be the major component of the toner. Charge carriers, of course, are well known to those having ordinary skill in the art and typically are polymer-coated metal particles. The identities and amounts of such additional components in the colored composition are well known to one of ordinary skill in the art. Further, the toner of the present invention, can also include a molecular includant as described above.

When the colored composition is employed as a toner for an electrophotographic process, several variations are possible and come within the scope of the present invention. For example, the composition-based toner can be used to form a first image on a virgin paper sheet. The sheet then can be recycled by exposing the sheet to ultraviolet radiation in accordance with the present invention to render the colorant, and, as a consequence, the composition, colorless. A second image then can be formed on the sheet. The second image can be formed from a standard, known toner, or from a composition-based toner which is either the same as or different from the composition-based toner which was used to form the first image. If a composition-based toner is

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thin film by means of a glass microscope slide. Each steel plate was 3 x 5 inches (7.6 cm x 12.7 cm) and was obtained from Q-Panel Company, Cleveland, Ohio. The film on the steel plate was estimated to have a thickness of the order of 10-20 micrometers.

5           In every instance, the colorant was Malachite Green oxalate (Aldrich Chemical Company, Inc., Milwaukee, Wisconsin), referred to hereinafter as Colorant A for convenience. The ultraviolet radiation transorber ("UVRT") consisted of one or more of Irgacure® 500 ("UVRT A"),  
10           Irgacure® 651 ("UVRT B"), and Irgacure® 907 ("UVRT C"), each of which was described earlier and is available from Ciba-Geigy Corporation, Hawthorne, New York. The polymer was one of the following: an epichlorohydrin-bisphenol A epoxy resin ("Polymer A"), Epon® 1004F (Shell Oil Company,  
15           Houston, Texas); a poly(ethylene glycol) having a weight-average molecular weight of about 8,000 ("Polymer B"), Carbowax 8000 (Aldrich Chemical Company); and a poly(ethylene glycol) having a weight-average molecular weight of about 4,600 ("Polymer C"), Carbowax 4600 (Aldrich Chemical Company). A control film  
20           was prepared which consisted only of colorant and polymer. The compositions of the films are summarized in Table 1.

**Table 1**  
**Compositions of Films Containing**  
**Colorant and Ultraviolet Radiation Transorber**  
**("UVRT")**

Film	<u>Colorant</u>		<u>UVRT</u>		<u>Polymer</u>	
	<u>Type</u>	<u>Parts</u>	<u>Type</u>	<u>Parts</u>	<u>Type</u>	<u>Parts</u>
A	A	1	A	6	A	90
			C	4		
B	A	1	A	12	A	90
			C	8		
C	A	1	A	18	A	90
			C	12		
D	A	1	A	6	A	90
			B	4		
E	A	1	B	30	A	70
F	A	1	--	--	A	100
G	A	1	A	6	B	90
			C	4		
H	A	1	B	10	C	90

While still on the steel plate, each film was exposed to ultraviolet radiation. In each case, the steel plate having the film sample on its surface was placed on a moving conveyor belt having a variable speed control. Three different ultraviolet radiation sources, or lamps, were used. Lamp A was a 222-nanometer excimer lamp and Lamp B was a 308-nanometer excimer lamp, as already described. Lamp C was a fusion lamp system having a "D" bulb (Fusion Systems Corporation, Rockville, Maryland). The excimer lamps were organized in banks of four cylindrical lamps having a length of about 30 cm, with the lamps being oriented normal to the direction of motion of the belt. The lamps were cooled by circulating water through a centrally located or inner tube of the lamp and, as a consequence, they operated at a relatively low temperature. i.e., about 50°C.

The power density at the lamp's outer surface typically is in the range of from about 4 to about 20 joules per square meter ( $J/m^2$ ).

However, such range in reality merely reflects the capabilities of current excimer lamp power supplies; in the future, higher power densities may be practical. With Lamps A and B, the distance from the lamp to the film sample was 4.5 cm and the belt was set to move at 20 ft/min (0.1 m/sec). With Lamp C, the belt speed was 14 ft/min (0.07 m/sec) and the lamp-to-sample distance was 10 cm. The results of exposing the film samples to ultraviolet radiation are summarized in Table 2. Except for Film F, the table records the number of passes under a lamp which were required in order to render the film colorless. For Film F, the table records the number of passes tried, with the film in each case remaining colored (no change).

**Table 2**  
**Results of Exposing Films Containing**  
**Colorant and Ultraviolet Radiation Transorber (UVRT)**  
**to Ultraviolet Radiation**

<u>Film</u>	<u>Excimer Lamp</u>		<u>Fusion Lamp</u>
	<u>Lamp A</u>	<u>Lamp B</u>	
A	3	3	15
B	2	3	10
C	1	3	10
D	1	1	10
E	1	1	1
F	5	5	10
G	3	--	10
H	3	--	10

### **EXAMPLE 2**

This example describes the preparation of solid colored compositions adapted to be utilized as toners in an electrophotographic process. In every instance, the toner

included Colorant A as described in Example 1; a polymer, DER 667, an epichlorohydrin-bisphenol A epoxy resin (Polymer D), Epon® 1004F (Dow Chemical Company, Midland, Michigan); and a charge carrier. Carrier A, which consisted of a very finely divided polymer-coated metal. The ultraviolet radiation transorber (UVRT) consisted of one or more of UVRT B from Example 1, Irgacure® 369 (UVRT D), and Irgacure® 184 (UVRT E); the latter two transorbers were described earlier and are available from Ciba-Geigy Corporation, Hawthorne, New York. In one case, a second polymer also was present, styrene acrylate 1221, a styrene-acrylic acid copolymer (Hercules Incorporated, Wilmington, Delaware).

To prepare the toner, colorant, ultraviolet radiation transorber, and polymer were melt-blended in a Model 3VV 800E, 3 inch x 7 inch (7.6 cm x 17.8 cm) two-roll research mill (Farrel Corporation, Ansonia, Connecticut). The resulting melt-blend was powdered in a Mikropul hammermill with a 0.010-inch herringbone screen (R. D. Kleinfeldt, Cincinnati, Ohio) and then sieved for proper particle sizes in a Sturtevant, air two-inch micronizer (R. D. Kleinfeldt) to give what is referred to herein as a pretoner. Charge carrier then was added to the pretoner and the resulting mixture blended thoroughly. Table 3 summarizes the compositions of the pretoners and Table 4 summarizes the compositions of the toners.

**Table 3**  
**Summary of Pretoner Compositions**

	<u>Pretoner</u>	<u>Colorant</u> <u>A (g)</u>	<u>UVRT</u>		<u>Polymer</u>	
			<u>Type</u>	<u>g</u>	<u>Type</u>	<u>g</u>
5	A	1	D	20	D	80
	B	1	B	20	D	80
	C	1	B	10	D	80
			D	10		
10	D	1	B	6.9	D	40
			D	6.6	E	40
			E	6.6		

**Table 4**  
**Summary of Toner Compositions**

	<u>Toner</u>	<u>Pretoner</u>		<u>Charge</u>
		<u>Type</u>	<u>g</u>	<u>Carrier (g)</u>
20	A	A	8.4	210
	B	B	8.4	210
	C	C	8.4	210
	D	D	8.4	210

Each toner was placed separately in a Sharp Model ZT-50TD1 toner cartridge and installed in either a Sharp Model Z-76 or a Sharp Model Z-77 xerographic copier (Sharp Electronics Corporation, Mahwah, New Jersey). Images were made in the usual manner on bond paper (Neenah Bond). The image-bearing sheets then were exposed to ultraviolet radiation from Lamp B as described in Example 1. In each case, the image was rendered colorless with one pass.

### EXAMPLE 3

This example describes the preparation of a  $\beta$ -cyclodextrin molecular inclusion having (1) an ultraviolet radiation transorbiter covalently bonded to the cyclodextrin outside of the cavity of the cyclodextrin and (2) a colorant associated with the cyclodextrin by means of hydrogen bonds and/or van der Waals forces.

#### A. Friedel-Crafts Acylation of Transorbiter

A 250-ml. three-necked, round-bottomed reaction flask was fitted with a condenser and a pressure-equalizing addition funnel equipped with a nitrogen inlet tube. A magnetic stirring bar was placed in the flask. While being flushed with nitrogen, the flask was charged with 10 g (0.05 mole) of 1-hydroxycyclohexyl phenyl ketone (Irgacure® 184, Ciba-Geigy Corporation, Hawthorne, New York), 100 ml of anhydrous tetrahydrofuran (Aldrich Chemical Company, Inc., Milwaukee, Wisconsin), and 5 g (0.05 mole) of succinic anhydride (Aldrich). To the continuously stirred contents of the flask then was added 6.7 g of anhydrous aluminum chloride (Aldrich). The resulting reaction mixture was maintained at about 0°C in an ice bath for about one hour, after which the mixture was allowed to warm to ambient temperature for two hours. The reaction mixture then was poured into a mixture of 500 ml of ice water and 100 ml of diethyl ether. The ether layer was removed after the addition of a small amount of sodium chloride to the aqueous phase to aid phase separation. The ether layer was dried over anhydrous magnesium sulfate. The ether was removed under reduced pressure, leaving 12.7 g (87 percent) of a white crystalline powder. The material was shown to be 1-hydroxycyclohexyl 4-(2-carboxyethyl)carbonylphenyl ketone by nuclear magnetic resonance analysis.



B. Preparation of Acylated Transorber Acid Chloride

A 250-ml round-bottomed flask fitted with a condenser was charged with 12.0 g of 1-hydroxycyclohexyl 4-(2-carboxyethyl)carbonylphenyl ketone (0.04 mole), 5.95 g (0.05 mole) of thionyl chloride (Aldrich), and 50 ml of diethyl ether. The resulting reaction mixture was stirred at 30°C for 30 minutes, after which time the solvent was removed under reduced pressure. The residue, a white solid, was maintained at 0.01 Torr for 30 minutes to remove residual solvent and excess thionyl chloride, leaving 12.1 g (94 percent) of 1-hydroxycyclohexyl 4-(2-chloroformylethyl)carbonylphenyl ketone.

C. Covalent Bonding of Acylated Transorber to Cyclodextrin

A 250-ml, three-necked, round-bottomed reaction flask containing a magnetic stirring bar and fitted with a thermometer, condenser, and pressure-equalizing addition funnel equipped with a nitrogen inlet tube was charged with 10 g (9.8 mmole) of  $\beta$ -cyclodextrin (American Maize-Products Company, Hammond, Indiana), 31.6 g (98 mmole) of 1-hydroxycyclohexyl 4-(2-chloroformylethyl)carbonylphenyl ketone, and 100 ml of N,N-dimethylformamide while being continuously flushed with nitrogen. The reaction mixture was heated to 50°C and 0.5 ml of triethylamine added. The reaction mixture was maintained at 50°C for an hour and allowed to cool to ambient temperature. In this preparation, no attempt was made to isolate the product, a  $\beta$ -cyclodextrin to which an ultraviolet radiation transorber had been covalently coupled (referred to hereinafter for convenience as  $\beta$ -cyclodextrin-transorber).

The foregoing procedure was repeated to isolate the product of the reaction. At the conclusion of the procedure as described, the reaction mixture was concentrated in a rotary evaporator to roughly 10 percent of the original volume. The residue was poured into ice water to which sodium chloride then was added to force the product out of solution. The resulting precipitate was isolated by filtration and washed with diethyl

ether. The solid was dried under reduced pressure to give 24.8 g of a white powder. In a third preparation, the residue remaining in the rotary evaporator was placed on top of an approximately 7.5-cm column containing about 15 g of silica gel. The residue was eluted with N,N-dimethylformamide, with the eluant being monitored by means of Whatman® Flexible-Backed TLC Plates (Catalog No. 05-713-161, Fisher Scientific, Pittsburgh, Pennsylvania). The eluted product was isolated by evaporating the solvent. The structure of the product was verified by nuclear magnetic resonance analysis.

*D. Association of Colorant with Cyclodextrin-Transorber-Preparation of Colored Composition*

To a solution of 10 g (estimated to be about 3.6 mmole) of beta-cyclodextrin-transorber in 150 ml of N,N-dimethylformamide in a 250-ml round-bottomed flask was added at ambient temperature 1.2 g (3.6 mmole) of Malachite Green oxalate (Aldrich Chemical Company, Inc., Milwaukee, Wisconsin), referred to hereinafter as Colorant A for convenience. The reaction mixture was stirred with a magnetic stirring bar for one hour at ambient temperature. Most of the solvent then was removed in a rotary evaporator and the residue was eluted from a silica gel column as already described. The beta-cyclodextrin-transorber Colorant A inclusion complex moved down the column first, cleanly separating from both free Colorant A and beta-cyclodextrin-transorber. The eluant containing the complex was collected and the solvent removed in a rotary evaporator. The residue was subjected to a reduced pressure of 0.01 Torr to remove residual solvent to yield a blue-green powder.

*E. Mutation of Colored Composition*

The beta-cyclodextrin-transorber Colorant A inclusion complex was exposed to ultraviolet radiation from two different lamps, Lamps A and B. Lamp A was a 222-nanometer

excimer lamp assembly organized in banks of four cylindrical lamps having a length of about 30 cm. The lamps were cooled by circulating water through a centrally located or inner tube of the lamp and, as a consequence, they operated at a relatively low temperature, i.e., about 50°C. The power density at the lamp's outer surface typically is in the range of from about 4 to about 20 joules per square meter ( $J/m^2$ ). However, such range in reality merely reflects the capabilities of current excimer lamp power supplies: in the future, higher power densities may be practical. The distance from the lamp to the sample being irradiated was 4.5 cm. Lamp B was a 500-watt Hanovia medium pressure mercury lamp (Hanovia Lamp Co., Newark, New Jersey). The distance from Lamp B to the sample being irradiated was about 15 cm.

A few drops of an N,N-dimethylformamide solution of the beta-cyclodextrin-transorber Colorant A inclusion complex were placed on a TLC plate and in a small polyethylene weighing pan. Both samples were exposed to Lamp A and were decolorized (mutated to a colorless state) in 15-20 seconds. Similar results were obtained with Lamp B in 30 seconds.

A first control sample consisting of a solution of Colorant A and beta-cyclodextrin in N,N-dimethylformamide was not decolorized by Lamp A. A second control sample consisting of Colorant A and 1-hydroxycyclohexyl phenyl ketone in N,N-dimethylformamide was decolorized by Lamp A within 60 seconds. On standing, however, the color began to reappear within an hour.

To evaluate the effect of solvent on decolorization, 50 mg of the beta-cyclodextrin-transorber Colorant A inclusion complex was dissolved in 1 ml of solvent. The resulting solution or mixture was placed on a glass microscope slide and exposed to Lamp A for 1 minute. The rate of decolorization, i.e., the time to render the sample colorless, was directly proportional to the solubility of the complex in the solvent, as summarized below.

Solvent	Solubility	Decolorization Time
N,N-Dimethylformamide	Poor	1 minute
Dimethylsulfoxide	Soluble	<10 seconds
Acetone	Soluble	<10 seconds
Hexane	Insoluble	--
Ethyl Acetate	Poor	1 minute

5 Finally, 10 mg of the beta-cyclodextrin-transorber Colorant A inclusion complex were placed on a glass microscope slide and crushed with a pestle. The resulting powder was exposed to Lamp A for 10 seconds. The powder turned colorless. Similar results were obtained with lamp B, but at a slower rate.

#### EXAMPLE 4

10 Because of the possibility in the preparation of colored composition described in Example 3 for the acylated transorber acid chloride to at least partially occupy the cavity of the cyclodextrin, to the partial or complete exclusion of colorant, a modified preparative procedure was carried out. Thus, this  
15 example describes the preparation of a beta-cyclodextrin molecular includant having (1) a colorant at least partially included within the cavity of the cyclodextrin and associated therewith by means of hydrogen bonds and/or van der Waals forces and (2) an ultraviolet radiation transorber covalently  
20 bonded to the cyclodextrin outside of the cavity of the cyclodextrin.

##### A. Association of Colorant with a Cyclodextrin

25 To a solution of 10.0 g (9.8 mmole) of beta-cyclodextrin in 150 ml of N,N-dimethylformamide was added 3.24 g (9.6 mmoles) of Colorant A. The resulting solution was stirred at ambient temperature for one hour. The reaction solution was concentrated under reduced pressure in a rotary

evaporator to a volume about one-tenth of the original volume. The residue was passed over a silica gel column as described in Part C of Example 1. The solvent in the eluant was removed under reduced pressure in a rotary evaporator to give 12.4 g of a blue-green powder, beta-cyclodextrin Colorant A inclusion complex.

*B. Covalent Bonding of Acylated Transorber to Cyclodextrin Colorant Inclusion Complex - Preparation of Colored Composition*

A 250-ml. three-necked, round-bottomed reaction flask containing a magnetic stirring bar and fitted with a thermometer, condenser, and pressure-equalizing addition funnel equipped with a nitrogen inlet tube was charged with 10 g (9.6 mmole) of beta-cyclodextrin Colorant A inclusion complex, 31.6 g (98 mmoles) of 1-hydroxycyclohexyl 4-(2-chloroformylethyl)carbonylphenyl ketone prepared as described in Part B of Example 1, and 150 ml of N,N-dimethylformamide while being continuously flushed with nitrogen. The reaction mixture was heated to 50°C and 0.5 ml of triethylamine added. The reaction mixture was maintained at 50°C for an hour and allowed to cool to ambient temperature. The reaction mixture then was worked up as described in Part A. above, to give 14.2 g of beta-cyclodextrin-transorber Colorant A inclusion complex, a blue-green powder.

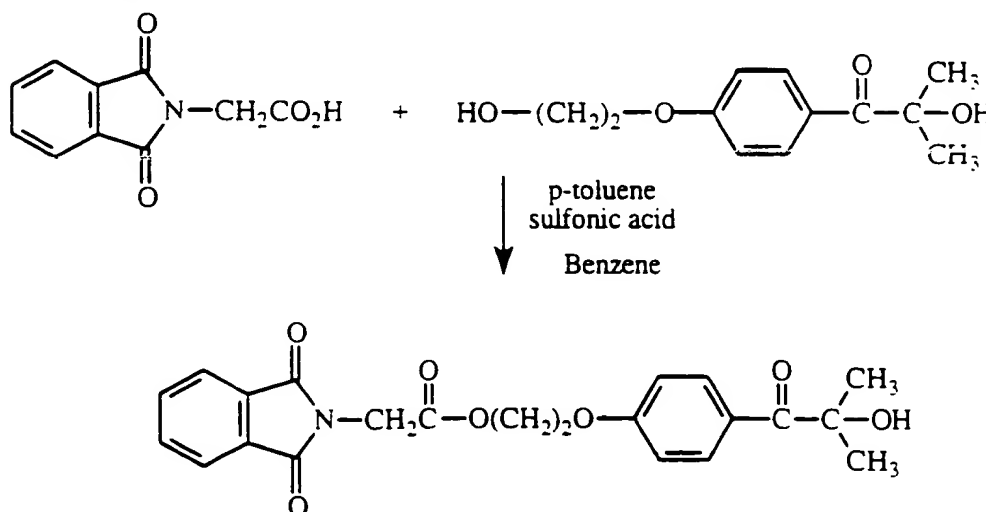
*C. Mutation of Colored Composition*

The procedures described in Part E of Example 1 were repeated with the beta-cyclodextrin-transorber Colorant A inclusion complex prepared in part B, above, with essentially the same results.

### EXAMPLE 5

This Example describes a method of preparing an ultraviolet radiation transorber designated phthaloylglycine-2959.

5       The following was admixed in a 250ml 3-necked round bottomed flask fitted with a Dean & Stark adapter with condenser and two glass stoppers: 20.5g (0.1mole) of the wavelength selective sensitizer, phthaloylglycine (Aldrich); 24.6g (0.1mole) of the photoreactor, DARCUR 2959 (Ciba-Geigy, Hawthorne, NY); 100 ml of benzene (Aldrich); and 0.4g p-toluene sulfonic acid (Aldrich). The mixture was heated at reflux for 3 hours after which time 1.8 ml of water was collected. The solvent was removed under reduced pressure to give 43.1g of white powder. The powder was recrystallized from 30% ethyl acetate in hexane (Fisher) to yield 40.2g (93%) of a white crystalline powder having a melting point of 153-4°C. The reaction is summarized as follows:



20       The resulting product, designated phthaloyl glycine-2959, had the following physical parameters:

IR [Nujol Muu]  $\nu_{\text{max}}$  3440, 1760, 1740, 1680, 1600  $\text{cm}^{-1}$

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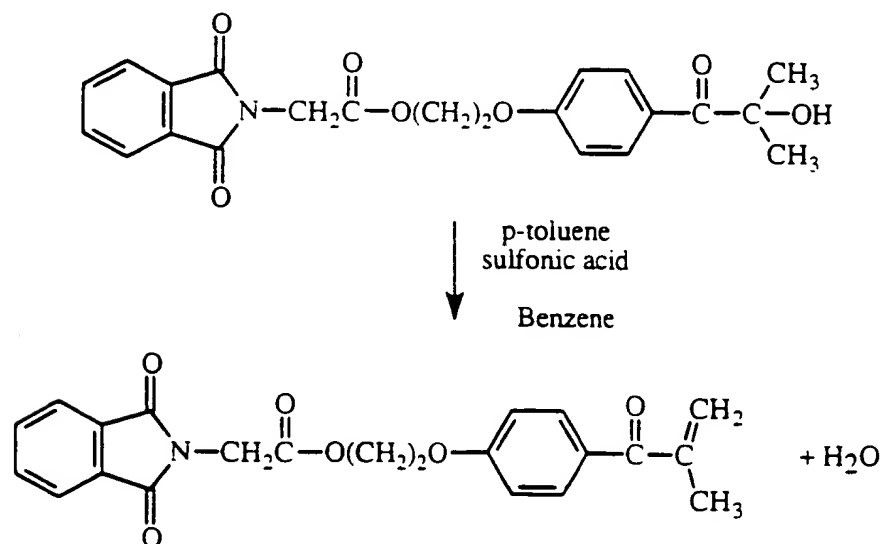
$^1\text{H}$ NMR [ $\text{CDCl}_3$ ]  $\delta$ ppm 1.64[s], 4.25[m], 4.49[m], 6.92[m], 7.25[m], 7.86[m], 7.98[m], 8.06[m] ppm

5

**EXAMPLE 6**

This Example describes a method of dehydrating the phthaloylglycine-2959 produced in Example 5.

The following was admixed in a 250ml round bottomed flask fitted with a Dean & Stark adaptor with condenser: 21.6g (0.05 mole) phthaloylglycine-2959; 100ml of anhydrous benzene (Aldrich); and 0.1g p-toluene sulfonic acid (Aldrich). The mixture was refluxed for 3 hours. After 0.7ml of water had been collected in the trap, the solution was then removed under vacuum to yield 20.1g (97%) of a white solid. The solid was used without further purification. The reaction is summarized as follows:



The resulting reaction product had the following physical parameters:

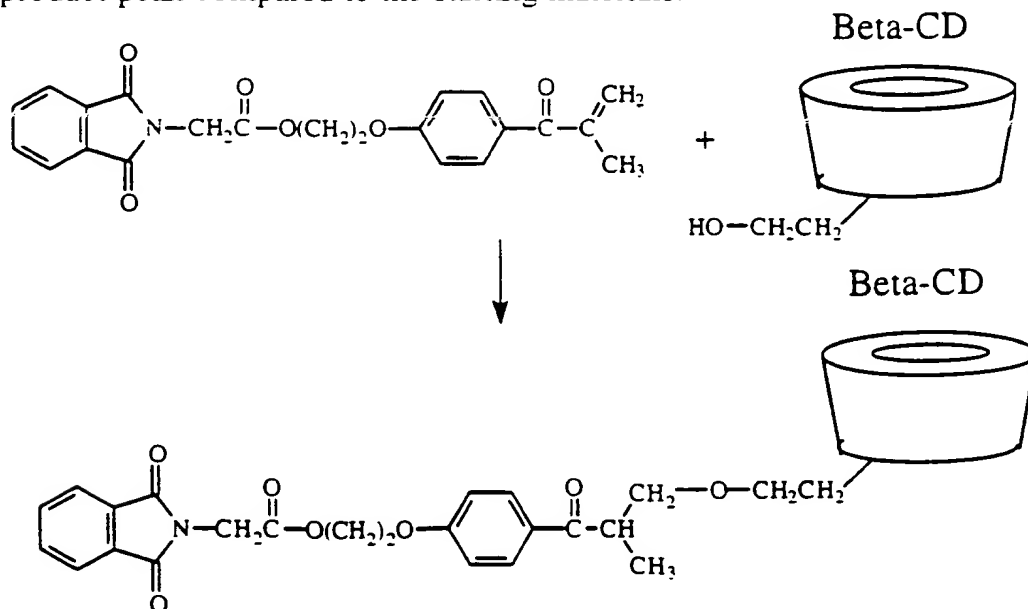
20

IR (NUJOL)  $\nu_{\text{max}}$   $1617\text{cm}^{-1}$  (C=C=O)

### EXAMPLE 7

This Example describes a method of producing a beta-cyclodextrin having dehydrated phthaloylglycine-2959 groups from Example 6 covalently bonded thereto.

The following was admixed in a 100ml round bottomed Flask: 5.0g (4mmole) beta-cyclodextrin (American Maize Product Company, Hammond, Indiana) (designated beta-CD in the following reaction); 8.3g (20 mmole) dehydrated phthaloylglycine-2959; 50ml of anhydrous DMF; 20ml of benzene; and 0.01g p-toluenesulfonyl chloride (Aldrich). The mixture was chilled in a salt/ice bath and stirred for 24 hours. The reaction mixture was poured into 150ml of weak sodium bicarbonate solution and extracted three times with 50ml ethyl ether. The aqueous layer was then filtered to yield a white solid comprising the beta-cyclodextrin with phthaloylglycine-2959 group attached. A yield of 9.4g was obtained. Reverse phase TLC plate using a 50:50 DMF:acetonitrile mixture showed a new product peak compared to the starting materials.





Of course, the beta-cyclodextrin molecule has several primary alcohols and secondary alcohols with which the phthaloylglycine-2959 can react. The above representative reaction only shows a single phthaloylglycine-2959 molecule for illustrative purposes.

### EXAMPLE 8

This example describes a method of associating a colorant and an ultraviolet radiation transorber with a molecular includant. More particularly, this Example describes a method of associating the colorant crystal violet with the molecular includant beta-cyclodextrin covalently bonded to the ultraviolet radiation transorber phthaloylglycine-2959 of Example 7.

The following was placed in a 100ml beaker: 4.0 g beta-cyclodextrin having a dehydrated phthaloylglycine-2959 group; and 50ml of water. The water was heated to 70°C at which point the solution became clear. Next, 0.9g (2.4 mmole) crystal violet (Aldrich Chemical Company, Milwaukee, WI) was added to the solution, and the solution was stirred for 20 minutes. Next, the solution was then filtered. The filtrand was washed with the filtrate and then dried in a vacuum oven at 84°C. A violet-blue powder was obtained having 4.1g (92%) yield. The resulting reaction product had the folowing physical parameters:

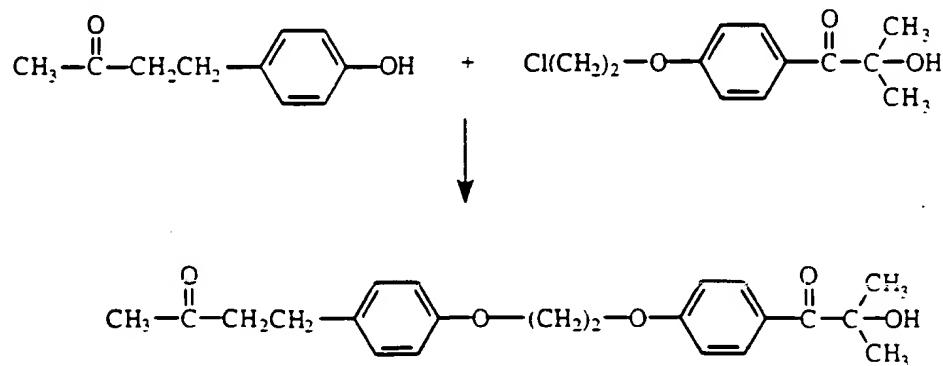
U.V. Spectrum DMF  $\Lambda_{\max}$  610nm (cf cv  $\Lambda_{\max}$  604nm)

### EXAMPLE 9

This Example describes a method of producing the ultraviolet radiation transorber 4(4-hydroxyphenyl) butan-2-one-2959 (chloro substituted) .

The following was admixed in a 250ml round bottomed flask fitted with a condensor and magnetic stir bar: 17.6g (0.1mole) of the wavelength selective sensitizer, 4(4-

hydroxyphenyl) butan-2-one (Aldrich Chemical Company, Milwaukee, WI); 26.4g (0.1 mole) of the photoreactor, chloro substituted DARCUR 2959 (Ciba-Geigy Corporation, Hawthorne, New York); 1.0 ml of pyridine (Aldrich Chemical Company, Milwaukee, WI); and 100ml of anhydrous tetrahydrofuran (Aldrich Chemical Company, Milwaukee, WI). The mixture was refluxed for 3 hours and the solvent partially removed under reduced pressure (60% taken off). The reaction mixture was then poured into ice water and extracted with two 50ml aliquots of diethyl ether. After drying over anhydrous magnesium sulfate and removal of solvent, 39.1g of white solid remained. Recrystallization of the powder from 30% ethyl acetate in hexane gave 36.7g (91%) of a white crystalline powder, having a melting point of 142-3°C. The reaction is summarized in the following reaction:



The resulting reaction product had the following physical parameters:

IR [Nujol Muu]  $\nu_{\text{max}}$  3460, 1760, 1700, 1620, 1600  $\text{cm}^{-1}$   
 $^1\text{H}$  [ $\text{CDCl}_3$ ]  $\delta$ ppm 1.62[s], 4.2[m], 4.5[m], 6.9[m] ppm

The ultraviolet radiation transorber produced in this Example, 4(4-hydroxyphenyl) butan-2-one-2959 (chloro substituted), may be associated with beta-cyclodextrin and a colorant such as crystal violet, using the methods described above in Examples 6 through 8 wherein 4(4-hydroxyphenyl) butan-2-

one-2959 (chloro substituted) would be substituted for the dehydrated phthaloylglycine-2959 in the methods in Examples 6 through 8.

5

### EXAMPLE 10

10 This Example demonstrates that the 222 nanometer excimer lamps illustrated in Figure 3 produce uniform intensity readings on a surface of a substrate 5.5 centimeters from the lamps, at the numbered locations, in an amount sufficient to mutate the colorant in the compositions of the present invention which are present on the surface of the substrate. The lamp 10 comprises a lamp housing 15 with four excimer lamp bulbs 20 positioned in parallel, the excimer lamp bulbs 20 are approximately 30 cm in length. The lamps are cooled by circulating water through a centrally located or inner tube (not shown) and, as a consequence, the lamps are operated at a relatively low temperature, i.e., about 50°C. The power density at the lamp's outer surface typically is in the range of from about 4 to about 20 joules per square meter (J/m<sup>2</sup>).

20 Table 5 summarizes the intensity readings which were obtained by a meter located on the surface of the substrate. The readings numbered 1, 4, 7, and 10 were located approximately 7.0 centimeters from the left end of the column as shown in Figure 3. The readings numbered 3, 6, 9, and 12 were located approximately 5.5 centimeters from the right end of the column as shown in Figure 3. The readings numbered 2, 5, 8, and 11 were centrally located approximately 17.5 centimeters from each end of the column as shown in Figure 3.

30

TABLE 5

Background ( $\mu$ W)	Reading (mW/cm <sup>2</sup> )
24.57	9.63
19.56	9.35
22.67	9.39
19.62	9.33
17.90	9.30
19.60	9.30
21.41	9.32
17.91	9.30
23.49	9.30
19.15	9.36
17.12	9.35
21.44	9.37

5

**EXAMPLE 11**

10 This Example demonstrates that the 222 nanometer excimer lamps illustrated in Figure 4 produce uniform intensity readings on a surface of a substrate 5.5 centimeters from the lamps, at the numbered locations, in an amount sufficient to mutate the colorant in the compositions of the present invention which are present on the surface of the substrate. The excimer lamp 10 comprises a lamp housing 15 with four excimer lamp bulbs 20 positioned in parallel, the excimer lamp bulbs 20 are approximately 30 cm in length. The lamps are cooled by circulating water through a centrally located or inner tube (not shown) and, as a consequence, the lamps are operated at a relatively low temperature, i.e., about 50°C. The power density at the lamp's outer surface typically is in the range of from about 4 to about 20 joules per square meter (J/m<sup>2</sup>).

20 Table 6 summarizes the intensity readings which were obtained by a meter located on the surface of the substrate. The

readings numbered 1, 4, and 7 were located approximately 7.0 centimeters from the left end of the columns as shown in Figure 4. The readings numbered 3, 6, and 9 were located approximately 5.5 centimeters from the right end of the columns as shown in Figure 4. The readings numbered 2, 5, 8 were centrally located approximately 17.5 centimeters from each end of the columns as shown in Figure 4.

TABLE 6

Background ( $\mu$ W)	Reading ( $\text{mW}/\text{cm}^2$ )
23.46	9.32
16.12	9.31
17.39	9.32
20.19	9.31
16.45	9.29
20.42	9.31
18.33	9.32
15.50	9.30
20.90	9.34

**EXAMPLE 12**

This Example demonstrates the intensity produced by the 222 nanometer excimer lamps illustrated in Figure 5, on a surface of a substrate, as a function of the distance of the surface from the lamps, the intensity being sufficient to mutate the colorant in the compositions of the present invention which are present on the surface of the substrate. The excimer lamp 10 comprises a lamp housing 15 with four excimer lamp bulbs 20 positioned in parallel, the excimer lamp bulbs 20 are approximately 30 cm in length. The lamps are cooled by circulating water through a centrally located or inner tube (not shown) and, as a consequence, the lamps are operated at a relatively low temperature, i.e., about 50°C. The power density at the lamp's outer surface typically is

in the range of from about 4 to about 20 joules per square meter ( $\text{J/m}^2$ ).

Table 7 summarizes the intensity readings which were obtained by a meter located on the surface of the substrate at position 1 as shown in Figure 5. Position 1 was centrally located approximately 17 centimeters from each end of the column as shown in Figure 5.

TABLE 7

<u>Distance</u> (cm)	<u>Background</u> ( $\mu\text{W}$ )	<u>Reading</u> ( $\text{mW/cm}^2$ )
5.5	18.85	9.30
6.0	15.78	9.32
10	18.60	9.32
15	20.90	9.38
20	21.67	9.48
25	19.86	9.69
30	22.50	11.14
35	26.28	9.10
40	24.71	7.58
50	26.95	5.20

Having thus described the invention, numerous changes and modifications hereof will be readily apparent to those having ordinary skill in the art without departing from the spirit or scope of the invention.

What is claimed is:

1. A colored composition comprising a mutable colorant and an ultraviolet radiation transorber.
2. The colored composition of Claim 1, further comprising a molecular includant.
3. The colored composition of Claim 2, wherein the molecular includant is selected from the group consisting of clathrates, zeolites, and cyclodextrins.
4. The colored composition of Claim 2, wherein the mutable colorant and the ultraviolet radiation transorber are associated with the molecular includant.
5. The colored composition of Claim 4, wherein the colorant is at least partially included within a cavity of the molecular includant.
6. The colored composition of Claim 4, wherein the ultraviolet radiation transorber is associated with the molecular includant outside of the cavity.
7. The colored composition of Claim 6, wherein the ultraviolet radiation transorber is covalently coupled to the molecular includant.

8. A method of mutating a colored composition wherein the colored composition comprises a mutable colorant and an ultraviolet radiation transorber, the method comprising the step of irradiating the colored composition with ultraviolet radiation at a dosage level sufficient to irreversibly mutate the colorant.

9. The method of Claim 8, wherein the colored composition further comprises a molecular includant.

10. The method of Claim 9, wherein the colorant and the ultraviolet radiation transorber are associated with the molecular includant.

11. The method of Claim 8, further comprising the step of applying the colored composition to a substrate before the colored composition is irradiated with ultraviolet radiation.

12. The method of Claim 11, in which the mutated colorant is stable.

13. The method of Claim 10, further comprising the step of applying the colored composition to a substrate before the colored composition is irradiated with ultraviolet radiation.

14. The method of Claim 13, in which the mutated colorant is stable.



15. A toner in an electrophotographic process comprising:
  - a mutable colorant;
  - an ultraviolet radiation transorber; and
  - a carrier for the colorant and the ultraviolet radiation transorber.
16. The toner of Claim 15, in which the carrier comprises a polymer.
17. The toner of Claim 15, wherein the composition further comprises a charge carrier.
18. The toner of Claim 15, wherein the ultraviolet transorber absorbs ultraviolet radiation with a wavelength of from about 100 to about 375 nanometers.
19. The solid colored composition of Claim 18, wherein the ultraviolet radiation is incoherent, pulsed ultraviolet radiation from a dielectric barrier discharge excimer lamp.
20. The toner of Claim 15, further comprising a molecular includant.
21. The toner of Claim 20, wherein the mutable colorant and the ultraviolet radiation transorber are associated with the molecular includant.
22. The toner of Claim 21, wherein the mutable colorant is at least partially included within a cavity of the molecular includant.

23. The toner of Claim 21, wherein the ultraviolet radiation transorber is covalently coupled to the molecular includant.

24. An electrophotographic process comprising the steps of:

creating an image on a photoreceptor surface;  
applying a toner to the photoreceptor surface to form a toner image which replicates the image, the toner comprising a mutable colorant, an ultraviolet radiation transorber, and a carrier;  
transferring the toner image to a substrate; and  
fixing the toner image to the substrate.

25. The electrophotographic process of Claim 24, wherein the carrier comprises a polymer.

26. The electrophotographic process of Claim 24, wherein the composition further comprises a charge carrier.

27. The electrophotographic process of Claim 24, wherein the ultraviolet radiation transorber absorbs ultraviolet light at a wavelength of from about 100 to about 375 nanometers.

28. The electrophotographic process of Claim 27, wherein the ultraviolet radiation is incoherent, pulsed ultraviolet radiation from a dielectric barrier discharge excimer lamp.

29. The electrophotographic process of Claim 24, wherein the toner further comprises a molecular includant.

30. The electrophotographic process of Claim 29, wherein the mutable colorant and the ultraviolet radiation transorber are associated with the molecular includant.

31. The electrophotographic process of Claim 30, wherein the mutable colorant is at least partially included within a cavity of the molecular includant.

32. The electrophotographic process of Claim 30, wherein the ultraviolet radiation transorber is covalently coupled to the molecular includant.

33. An electrophotographic process comprising the steps of:

- providing a substrate having a first image thereon which is formed by a first toner which comprises:

- a mutable colorant;

- an ultraviolet radiation transorber; and

- a carrier for the colorant and the ultraviolet radiation transorber;

- exposing the first image on the substrate to ultraviolet radiation at a dosage level sufficient to irreversibly mutate the colorant;
- creating a second image on a photoreceptor surface;

- applying a second toner to the photoreceptor surface to form a toner image which replicates the second image;

transferring the second toner image of the second image to the substrate; and  
fixing the second toner image to the substrate.

34. The electrophotographic process of Claim 33, wherein the carrier is a polymer.

35. The electrophotographic process of Claim 33, wherein the first toner further comprises a charge carrier.

36. The electrophotographic process of Claim 33, wherein the first toner further includes a molecular inculdant.

37. The electrophotographic process of Claim 33, wherein the ultraviolet radiation transorber absorbs ultraviolet radiation at a wavelength of from about 100 to about 375 nanometers.

38. The electrophotographic process of Claim 37, in which the ultraviolet radiation is incoherent, pulsed ultraviolet radiation from a dielectric barrier discharge excimer lamp.

39. The electrophotographic process of Claim 33, in which the second toner comprises:  
a second mutable colorant;  
a second ultraviolet radiation transorber; and  
a second carrier for the second colorant and the second ultraviolet radiation transorber.

40. The electrophotographic process of Claim 39, wherein the second carrier is a polymer.

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41. The electrophotographic process of Claim 39, wherein the second toner includes a charge carrier.

42. The electrophotographic process of Claim 39, wherein the second toner further includes a molecular includant.

43. The electrophotographic process of Claim 39, wherein the ultraviolet radiation has a wavelength of from about 100 to about 375 nanometers.

44. The electrophotographic process of Claim 43, wherein the ultraviolet radiation transorber absorbs ultraviolet radiation at a wavelength of from about 100 to about 375 nanometers.

45. A substrate having an image thereon that is formed by a colored composition, the colored composition comprising a mutable colorant and an ultraviolet radiation transorber.

46. The substrate of Claim 45, wherein the colored composition further comprises a molecular includant.

47. The substrate of Claim 46, wherein the molecular includant is selected from the group consisting of clathrates, zeolites, and cyclodextrins.

48. The substrate of Claim 46, wherein the mutable colorant and the ultraviolet radiation transorber are associated with the molecular includant.

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49. A substrate having an image thereon that is formed by an electrophotographic toner, the electrophotographic toner comprising a mutable colorant, an ultraviolet radiation transorber and a carrier for the colorant and the ultraviolet radiation transorber.

50. The substrate of Claim 49, wherein the carrier comprises a polymer.

51. The substrate of Claim 49, wherein the toner further comprises a charge carrier.

52. The substrate of Claim 49, wherein the toner further comprises a molecular includant.

53. The substrate of Claim 52, wherein the molecular includant is selected from the group consisting of clathrates, zeolites, and cyclodextrins.

54. The substrate of Claim 52, wherein the mutable colorant and the ultraviolet radiation transorber are associated with the molecular includant.

55. An ultraviolet radiation transorber which comprises, in combination, a wavelength-selective sensitizer and a photoreactor.

56. The ultraviolet radiation transorber of Claim 55, wherein the wavelength-selective sensitizer is covalently coupled to the photoreactor.

57. The ultraviolet radiation transorber of Claim 55, wherein the wavelength-selective sensitizer absorbs ultraviolet radiation having a wavelength of from about 100 to about 375 nanometers.

58. The ultraviolet radiation transorber of Claim 57, wherein the ultraviolet radiation is incoherent, pulsed ultraviolet radiation from a dielectric barrier discharge excimer lamp.

59. The ultraviolet radiation transorber of Claim 55, wherein the wavelength-selective sensitizer is selected from the group consisting of phthaloylglycine, and 4-(4-oxyphenyl)-2-butanone.

60. The ultraviolet radiation transorber of Claim 55, wherein the photoreactor is selected from the group consisting of [4-(2-hydroxyethoxy) phenyl]-2-hydroxy-2-methylpropan-1-one, and cyclohexyl-phenyl ketone ester.

61. The ultraviolet radiation transorber of Claim 55, which transorber is phthaloylglycyl-1-[4-(2-hydroxyethoxy) phenyl]-2-hydroxy-2-methylpropan-1-one.

62. The ultraviolet radiation transorber of Claim 55, which transorber is phthaloylglycyl-cyclohexyl-phenyl ketone ester.

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63. The ultraviolet radiation transorber of Claim 55, which transorber is 4-(4-oxyphenyl)-2-butanone-1-[4-(2-oxyethoxy)phenyl]-2-hydroxy-2-methyl-propan-1-one ester.

64. The ultraviolet radiation transorber of Claim 55, which transorber is 4-(4-oxyphenyl)-2-butanone-cyclohexyl-phenyl ketone ester.



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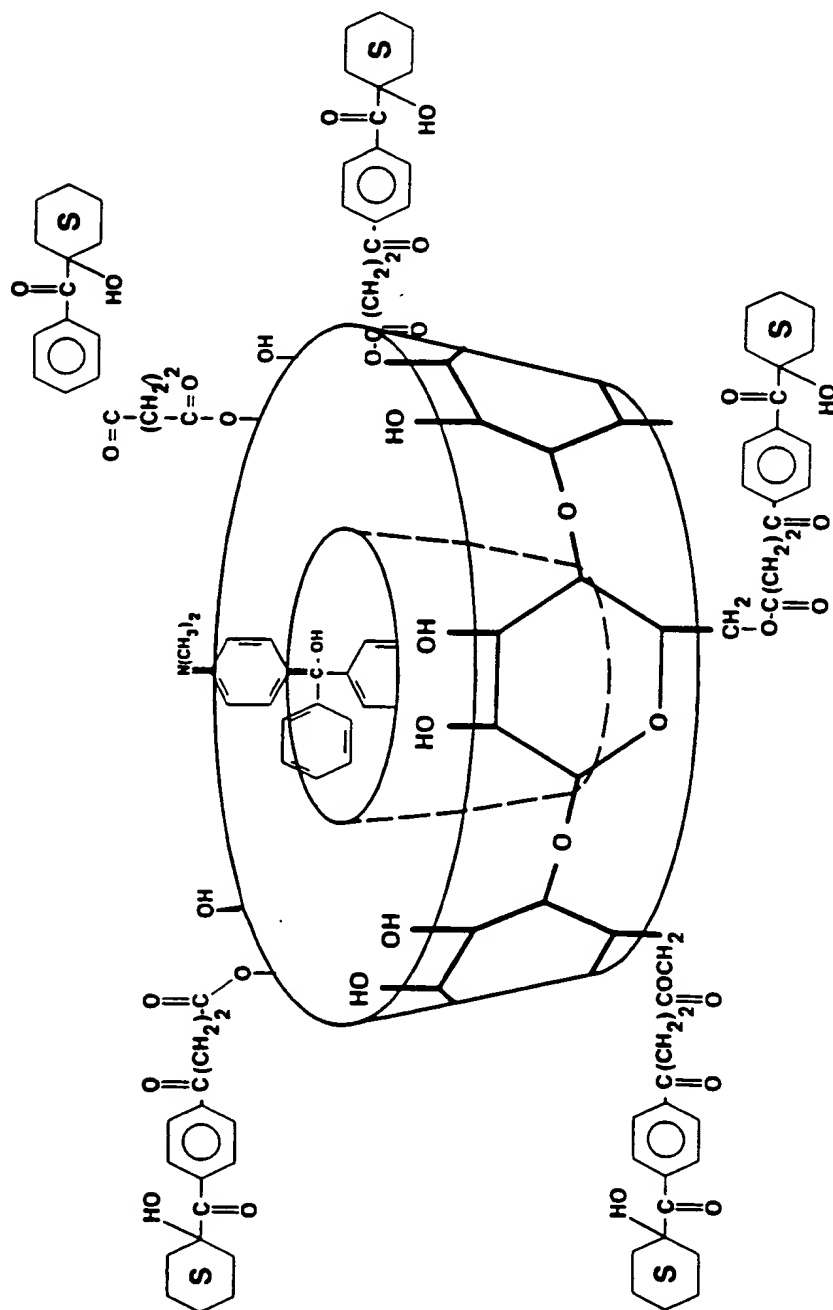


FIG. 1

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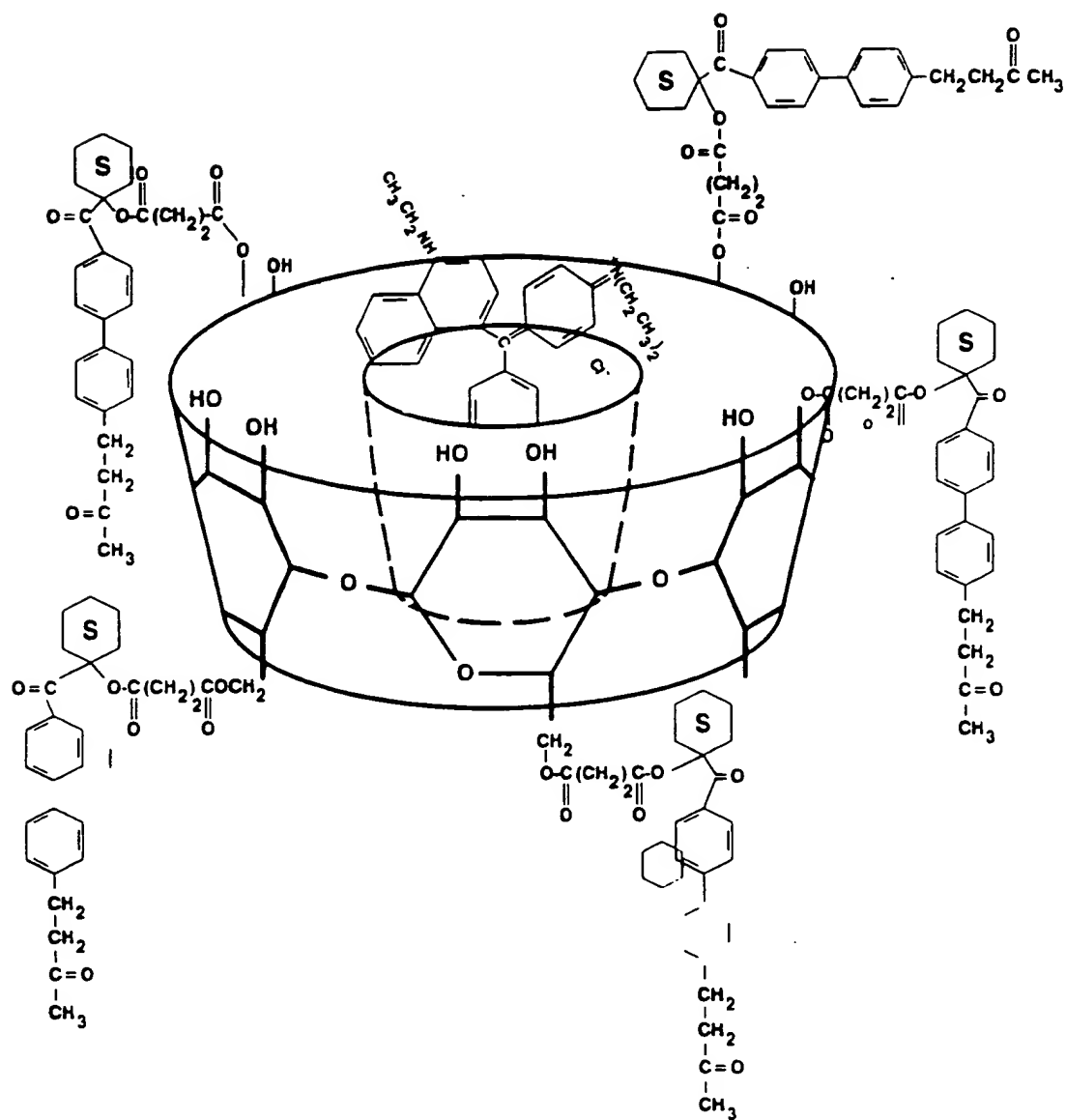
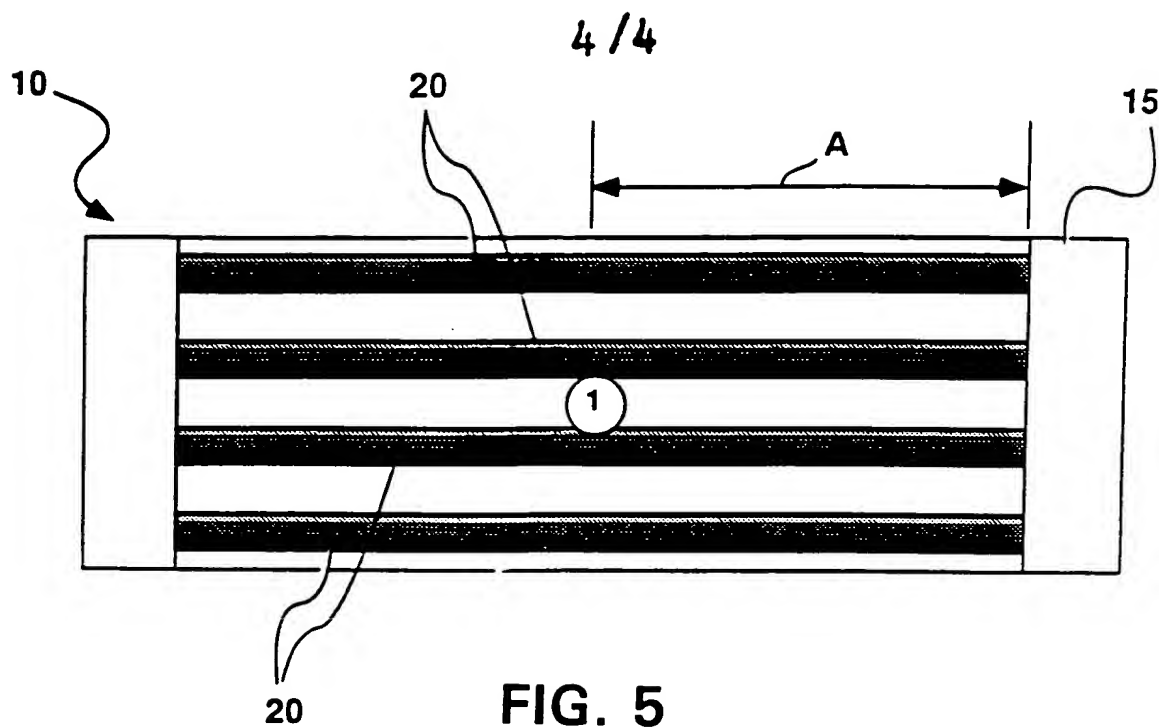


FIG. 2



3/4

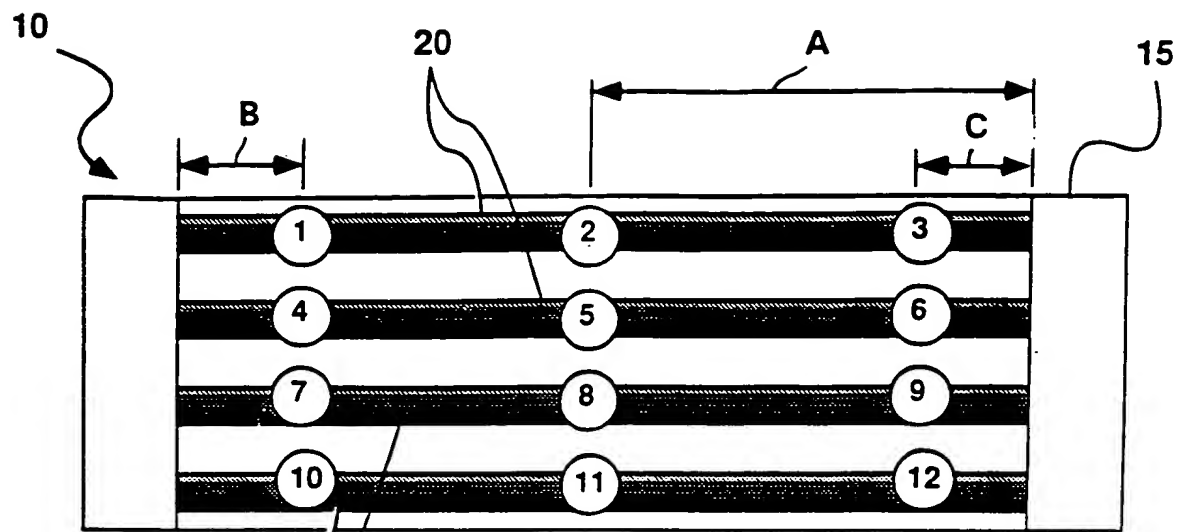


FIG. 3

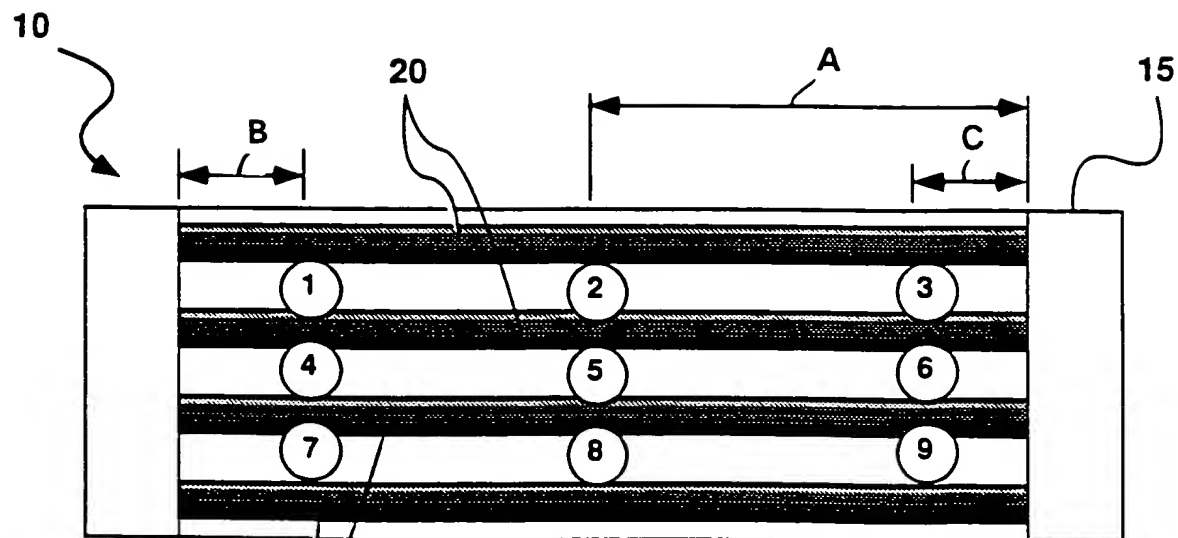


FIG. 4

# INTERNATIONAL SEARCH REPORT

International application No.  
PCT/US 94/08588

## A. CLASSIFICATION OF SUBJECT MATTER

IPC 6 G03G9/09

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 G03G G01C G03C G03F G11B B41M C08B

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO,A,93 06597 (EASTMAN KODAK) 1 April 1993 see page 18, line 12 - line 25 see page 23; table I see claims 9,10,17,24 ---	1
X	PATENT ABSTRACTS OF JAPAN vol. 13, no. 516 (C-656) 17 November 1989 & JP,A,01 210 477 (CANON INC) 24 August 1989 see abstract ---	1-3
X	DATABASE WPI Section Ch, Week 8404, Derwent Publications Ltd., London, GB; Class CH, AN 84-020629 [04] & JP,A,58 211 426 (SEKISUI PLASTICS KK) 8 December 1983 see abstract ---	1-3
-/--		

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

### \* Special categories of cited documents :

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- 'P' document published prior to the international filing date but later than the priority date claimed

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Date of the actual completion of the international search

30 November 1994

Date of mailing of the international search report

20.12.94

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2  
NL - 2280 HV Rijswijk  
Tel. (+ 31-70) 340-2040, Tx. 31 651 epo nl,  
Fax: (+ 31-70) 340-3016

Authorized officer

Vogt, C

## INTERNATIONAL SEARCH REPORT

International application No.  
PCT/US 94/08588

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT		
Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	PATENT ABSTRACTS OF JAPAN vol. 15, no. 406 (P-1263) 16 October 1991 & JP,A,03 163 566 (MITSUBISHI) 15 July 1991 see abstract ---	1,15,16
X	DATABASE WPI Section Ch, Week 9326, Derwent Publications Ltd., London, GB; Class CH, AN 93-209454 [26] & JP,A,5 134 447 (BANDO CHEM) 14 November 1991 see abstract ---	1,15,16, 24,25,45
A	DE,A,41 32 288 (DIGITAL STREAM) 23 April 1992 see column 5, line 1 - line 11 ---	8-46
X	US,A,3 799 773 (WATARAI ET AL.) 26 March 1974 see column 6; example 2 ---	8,11,45
X	EP,A,0 542 286 (BANDO CHEM) 19 May 1993  see page 12, line 48 - page 13, line 11 see claim 1 -----	1,15-18, 24-27, 45,55-57

# INTERNATIONAL SEARCH REPORT

Information on patent family members

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PCT/US 94/08588

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EP-A-0542286	19-05-93	JP-A- 5181308 JP-A- 5181310 JP-A- 5197198 US-A- 5362592 JP-A- 5241369	23-07-93 23-07-93 06-08-93 08-11-94 21-09-93